

Identification of the surface features in the electronic structure of Cr

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We studied the electronic structure of high quality Cr(110) films grown on W(110) surface employing photoemission spectroscopy. Experiments on the differently aged samples revealed distinct signatures of the surface and bulk features in the electronic structure. It is observed that the adsorbed oxygens form covalent bonds with the surface Cr atoms at higher temperatures, while they remain almost unreacted at low temperatures. In addition to the spin density wave transition induced band folding across the bulk Neél temperature, we discover a weakly dispersing sharp feature emerging near the Fermi level at low temperatures presumably due to correlation induced effects.

Unusual magnetism of elemental Cr led to its wide ranging applications involving recording media, high density storage media, magnetic sensors, giant magnetoresistance based devices etc. Enormous effort has been put forward to understand the exotic electronic properties of this system, which is crucial to have further developments in technological application of this material as well as involved fundamental science. Bulk Cr forms in bcc structure and is a good example of Fermi surface nesting driven antiferromagnet¹⁻³ exhibiting incommensurate spin density wave (ISDW) transition at 311 K that becomes commensurate via a spin-flip transition around 150 K. Various studies revealed several controversies in its electronic properties; for example, antiferromagnetic/ferromagnetic surface on antiferromagnetic bulk²⁻⁵, complex surface-bulk differences in the electronic structure⁵⁻⁸, orbital Kondo effect vs. shockley surface states⁸⁻¹¹, proximity to quantum criticality¹² etc. Contrasting scenario on the energy gap has also been reported such as signature of pseudogap¹³, direct multiple gaps¹⁴ in the ISDW phase. Manifestation of such multifaceted exoticity in a simple elemental system is remarkable and has continued to attract much attention in the fundamental science and technology for long.

Device fabrication based on such materials requires knowledge of the surface behavior - whether the bulk properties survives at the surface, if differs how much is the deviation, etc. In order to investigate the surface electronic structure critically, we studied the evolution of the electronic structure of Cr with temperature and aging. We prepared Cr(110) surface, which is antiferromagnetic and expected not to favor orbital Kondo resonance. This allows us to investigate the surface-bulk differences in the electronic structure solely due to surface termination induced effect without major change in their magnetism. Our results reveal surface and bulk character of various photoemission spectral features unambiguously and interesting evolution of the surface states on aging. Electron correlation is found to play important role in the electronic properties of this system.

The sample was prepared in an ultrahigh vacuum chamber (base pressure better than 1×10^{-10} Torr) by electron beam evaporation of Cr onto a clean W(110) surface. The details of the sample preparation and charac-

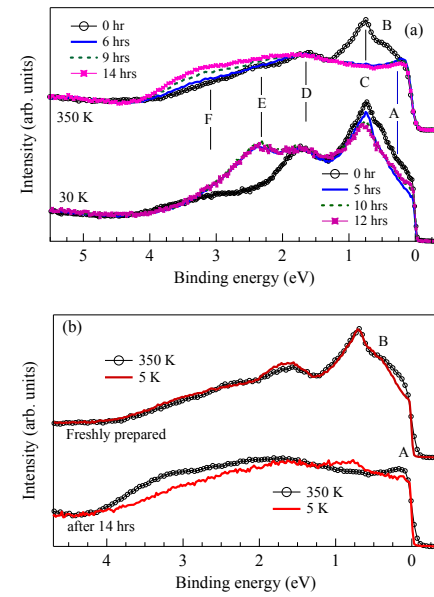


FIG. 1. (a) Aging of the normal emission spectra at 350 K and 30 K. (b) Normal emission spectra at 350 K and 5 K from freshly prepared sample (upper panel). The lower panel shows 14 hours aged spectrum at 350 K (open circles) and then cooled the same aged sample to 5 K (line).

terization is given in the supplementary materials. Angle resolved photoemission spectroscopic (ARPES) measurements were carried out using a Phoibos150 analyzer from Specs GmbH and monochromatic He I source ($h\nu = 21.2$ eV) with the momentum resolution fixed at $0.01 \times 2\pi/a$, where the lattice constant of Cr, a is 2.88 \AA . The x -ray photoemission spectroscopy (XPS) measurements were carried out with a monochromatic Al $K\alpha$ source. All these experiments were carried at a base pressure of about 1×10^{-10} Torr. The experiment temperature was achieved using an open cycle helium cryostat, LT-3M from Advanced Research Systems, USA.

First we investigate the evolution of the electronic structure with aging. Angle integrated photoemission

technique was employed with an acceptance angle of $\pm 15^\circ$ to enable quick collection of the data with good signal to noise ratio. The spectra collected at 350 K & 30 K from freshly prepared sample are shown in Fig. 1(a) after normalizing by the intensity around 6 eV binding energy. Each spectrum exhibits several features at the binding energies 0.2, 0.4, 0.7, 1.5, 2.4 & 3.2 eV - the features are denoted by A, B, C, D, E & F in the figure. The intensity between 0.3-1.2 eV binding energy range in the 350 K spectra decreases dramatically with time and becomes almost saturated within about 6 hours. Such spectral change with aging can be attributed to the suppression of intensities by the impurities adsorbed on the surface and/or bonded to the surface atoms. The intensities near the Fermi level, ϵ_F appear to remain uninfluenced by aging at 350 K. Curiously, a substantial decrease in intensity of A is observed at 30 K. Since aging influences the surface states most prominently, the feature A must be possessing significant surface character at 30 K. Such phenomena suggest a surface spectral weight transfer from higher binding energy regime to the vicinity of ϵ_F with the decrease in temperature and hence, the emergence of the surface character of the intensities around 0.2 eV at low temperatures.

Subsequent to the decrease of B and C in the 350 K spectra, the intensities of the features, E and F increase with aging. Employing XPS (shown in the supplementary data) we observed that the intensity of the oxygen 1s signal grows with time delay as often observed by us in various other studies¹⁵. Therefore, the spectral evolution observed here are attributed to the influence of oxygens on the surface states. The feature, E appears due to the non-bonding oxygen levels, and the features D & F correspond to the energy bands hybridized to oxygen 2p states. The scenario at 30 K is significantly different; in addition to large decrease in intensity in the vicinity of ϵ_F , intensity of the feature E becomes significantly intense within a very short time delay keeping the features D and F intensities almost unchanged. This suggests that the Cr-O bonding is less significant at low temperatures and the presence of large amount of adsorbed oxygen that leads to an enhancement of the non-bonding feature, E.

The temperature evolution of the electronic structure across the bulk Néel temperature of 311 K is investigated in Fig. 1(b). The 350 K and 5 K spectra obtained from the freshly prepared sample are compared in the upper panel of Fig. 1(b). Distinct decrease in intensity in the vicinity of ϵ_F is observed in addition to a small increase in intensity of the feature D. The surface features remain unchanged in this large temperature range due to the fact that the surface magnetic transition occurs at a higher temperature and the changes within the magnetically ordered phase is negligible^{5,16}. This is further verified by cooling down the 14 hours aged sample possessing primarily the bulk features near ϵ_F . The 350 K and 5 K spectra exhibit significant decrease in intensity near ϵ_F as a signature of antiferromagnetic transition¹⁷. Interestingly, the intensity around 0.7 eV (feature C) be-

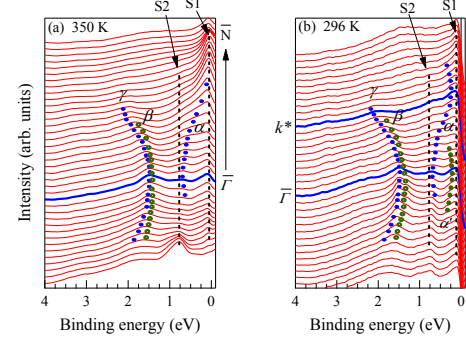


FIG. 2. ARPES data at (a) 350 K and (b) 296 K. symbols show the peak positions.

comes stronger along with a decrease in intensity beyond 1.5 eV binding energy. This corroborates the conclusions of less Cr-O bonded objects at 5 K due to less reactivity of oxygens at lower temperatures.

In order to investigate the band character of the above features, the energy band dispersions of Cr(110)/W(110) sample obtained by ARPES are shown in Figs. 2(a) and 2(b). Distinct signature of three energy bands denoted by α , β and γ are observed. These three energy bands possess behavior quite similar to the t_{2g} bands obtained from band structure calculations¹⁸⁻²⁰; the degeneracy of the t_{2g} bands at Γ is lifted due to the fact that He I photon energy ($h\nu = 21.2$ eV) corresponds to a k_z -value ($k_z \sim 1.7 \times 2\pi/c$; c is the lattice constant along (110) direction) away from the high symmetry point, Γ . Such photon energy dependence of the band dispersion will be absent for the surface bands, which is the primary focus of this study. There could be additional effect due to the strain arising from the differences in the lattice constants of Cr films with the W(110) substrate. The energy dispersion of the α band with d_{xy} (z -axis along the surface normal) symmetry makes an electron pocket around the Γ -point and resembles well to the theoretically calculated results¹⁸⁻²⁰.

In addition to the bulk bands, distinct signature of a weakly dispersive band is observed around 0.7 eV binding energy denoted by S2 in the figure, which is within the energy gap of the bulk bands α and β . Another almost non-dispersive feature denoted by S1 also appears near ϵ_F . These features are found to be significantly sensitive to aging as shown in Fig. 1 (features, A and C) indicating their surface character. The comparison of the experimental spectra at 296 K and 350 K in Figs. 2(a) and 2(b) reveals interesting evolution. While all the energy bands remain almost similar, the α band appears to fold back at k^* as shown in the figure - signature of band folding due to incommensurate SDW transition. In addition, a new feature denoted by α' appears near $\bar{\Gamma}$.

The temperature evolution of the features near ϵ_F as a function of temperature is shown in Fig. 3. In addition

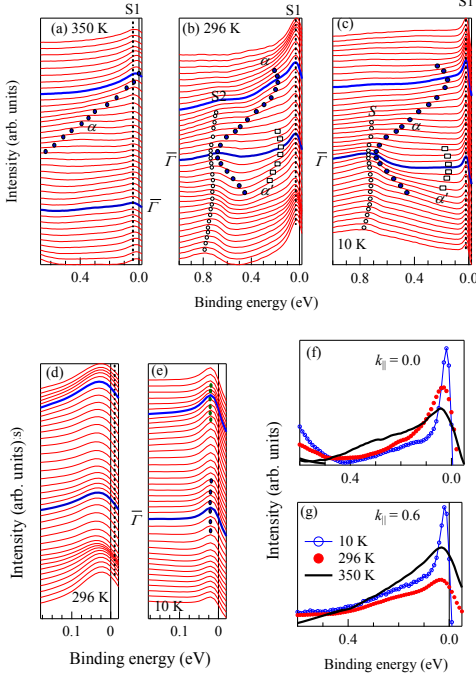


FIG. 3. Experimental energy bands at (a) 350 K, (b) 296 K and (c) 10 K. The energy distribution curves (EDC) with expanded energy scale at 296 K and 10 K are shown in (d) and (e), respectively. EDCs at different temperatures at (f) $k_{||} = 0.0$ and (g) $k_{||} = 0.6$.

to the band folding effect, the comparison of the spectra at 350 K, 296 K and 10 K exhibit emergence of a sharp feature around 15 meV below ϵ_F possessing weak dispersion. The distinct nature of this additional intensity is most evident in the energy distribution curves shown in Fig. 3(f) and 3(g). Moreover, it exhibits different trend in the change in intensities with temperature at Γ and k^* ($k_{||} = 0.6$) - the intensity at ϵ_F gradually increases with the decrease in temperature at Γ while the intensity at 296 K is the lowest at k^* .

Detailed temperature evolution of the features in the low temperature range (below 110 K) are shown in Fig. 4, where we show the energy distribution curves at $\bar{\Gamma}$ and $k_{||} = 1.0$. The features around 1.5 eV binding energy represent the intensities of the β & γ bands corresponding to the bulk electronic structure and exhibit enhancement in intensity with the decrease in temperature at $k_{||} = 1.0$, while it seems opposite at $\bar{\Gamma}$. Overall, the intensity increases at 1.5 eV as observed in the angle integrated spectra shown in Fig. 1(b) suggesting an enhancement of the local moment of the system within the magnetically ordered phase. The intensities at ϵ_F exhibit significant enhancement at low temperatures and asymmetry with respect to ϵ_F ²¹. This is shown in Figs. 4(c) and 4(d) after dividing the experimental spectra by the resolution broadened Fermi-distribution function.

It is clear that the electronic structure of one of the

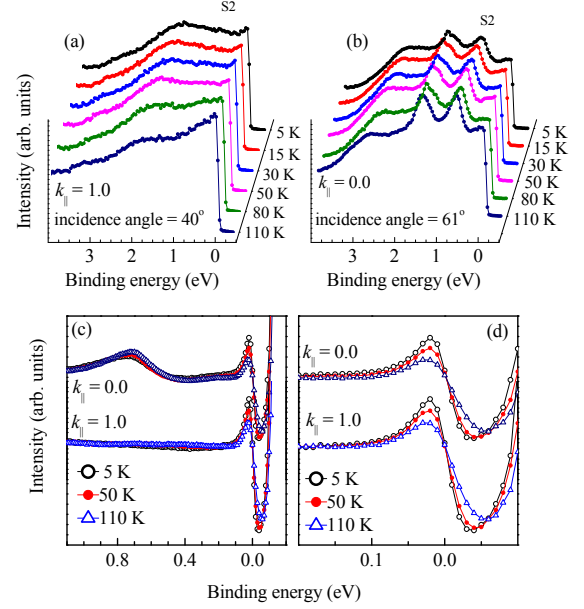


FIG. 4. Temperature evolution of EDC at (a) $k_{||} = 1.0$ and (b) $k_{||} = 0.0$. (c) and (d) show the spectral density of states near ϵ_F at different temperatures in an expanded energy scale.

most used elemental metal, Cr is quite complex. The results of our extensive experimental study unveil plethora of interesting scenarios, which have significant impact on application of this materials for future technological advancements. Firstly, we identify the surface features via reduction in intensity due to aging and observe that the degradation of the surface features of Cr film strongly depends on temperature. At low temperatures, we observe signature of adsorbed oxygen, which reduces the surface feature intensities. At elevated temperatures, the oxygens form bonding with the surface Cr atoms that enhances Cr spectral contributions at higher binding energies (around 3.2 eV) due to the bonding-antibonding splitting of the electronic states. The enhancement of the reactivity to surface impurities at higher temperature happens due to the thermal energy providing suitable activation for such reactions.

While the above results on aging of the Cr surface provide details of the surface stability, the spectral evolution due to adsorption/bonding of impurities with the surface atoms helps to identify the surface and bulk features in the electronic structure. There have been controversy on the surface character of the spectral feature at 0.7 eV binding energy denoted by S2 in Fig. 1. Substantial decrease in intensity with aging unambiguously indicates surface character of S2. The other important issue involves the observation of significant sensitivity of S1 to aging at 30 K and it's absence at 350 K. This suggests that the predominant surface character around 0.2 eV

becomes evident at low temperatures presumably due to the fact that the bulk contributions near ϵ_F diminishes significantly at low temperatures due to the formation of SDW gap making the relative surface contributions near ϵ_F discernible at low temperatures. In addition, there could be surface spectral weight transfer with the decrease in temperature.

Photoemission measurements at room temperature with varied angle of incident/emitted photon beam concluded Shockley type surface states with d_{z^2} character of S1⁸. In order to learn the orbital character of the growing intensities at low temperatures, we compare the spectra obtained at two geometries - the incident photon beam at 61° ($k_{||}=0.0$) and 40° ($k_{||}=1.0$) with respect to the surface normal. Thus, the $k_{||}=1.0$ case becomes slightly more favorable to probe $d_{xz}d_{yz}$ states and the d_{z^2} states becomes significantly less sensitive due to relatively more in-plane alignment of the light polarization vector. In Fig. 4(d), we observe that the intensity of the sharp feature at 15 meV becomes more intense in the $k_{||}=1.0$ spectra suggesting $d_{xz}d_{yz}$ character of the growing feature over the intensities of S1.

It is to note here that the studied Cr(110) surface is unlikely to exhibit orbital Kondo behavior as the surface is expected to be antiferromagnetic, while orbital Kondo effect corresponds to spin-ferromagnetic order²². In general, correlated electron systems such as rare-earths²³ and transition metal oxides²⁴ exhibit temperature reduction induced growth of the coherent feature at ϵ_F with respect to the intensities of the incoherent feature representing the correlation induced electronic states. The emergence of the sharp feature around 15 meV binding energy with the decrease in temperature observed here presumably suggests similar scenario in this system. Clearly, more studies are necessary to understand the complexity of the electronic structure of this system.

In summary, we have investigated the detailed electronic structure of high quality Cr(110) films grown on W(110) employing angle resolved photoemission spectroscopy. The aging of the sample surface helped to reveal the surface and bulk character of various spectral features. The adsorbed oxygens on the surface form bonds with the surface Cr atoms at temperatures close to room temperature, while they behave like adsorbed gas at low temperatures. The bulk electronic structure exhibits signature of band folding due to bulk spin density wave transition. There are two surface peaks around 0.2 eV and 0.7 eV binding energies. The temperature variation down to 5 K reveals emergence of an additional sharp

feature corresponding to the surface electronic structure. These results reveal the complex surface behavior of Cr, instability of the surface states with aging and the importance of electron correlation induced effect in the electronic structure, which are important to understand for its potential applications.

I. ACKNOWLEDGEMENTS

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